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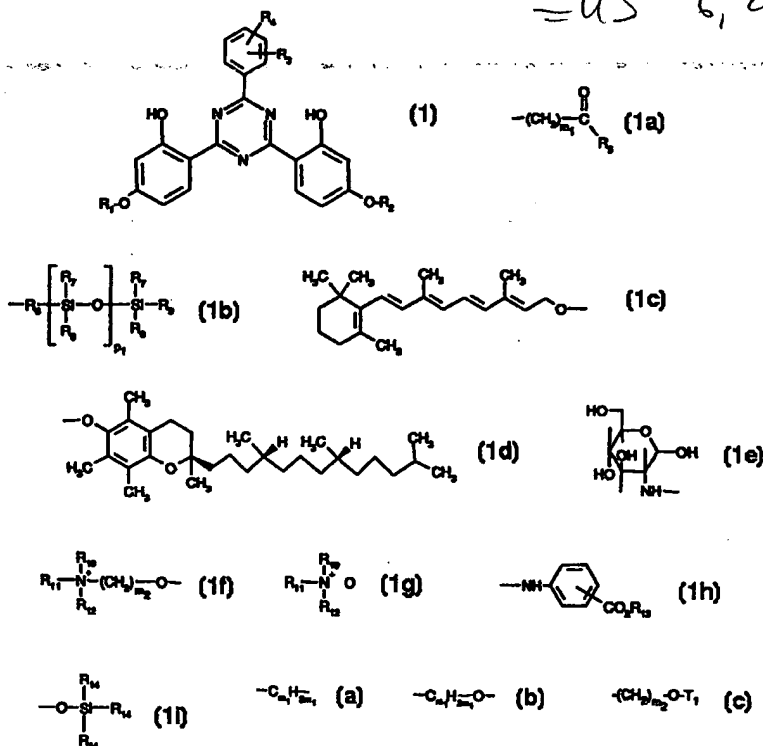
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(54) Title: COSMETIC USE OF BIS(RESORCINYL)TRIAZINE DERIVATIVES

(57) Abstract

A description is given of the use of bis(resorcinyl)triazines of formula (1) wherein R_1 and R_2 are each independently of the other hydrogen; C_1 - C_{18} alkyl; C_2 - C_{18} alkenyl; a radical of formula $-CH_2-CH(OH)-CH_2-O-T_1$; a radical of formula (1a); or a radical of formula (1b); R_3 and R_4 are each independently of the other hydrogen; or C_1 - C_5 alkyl; R_5 is hydroxy; C_1 - C_5 alkoxy which is unsubstituted or substituted by one or several OH groups; amino; mono- or di- C_1 - C_5 alkylamino; M; a radical of formula (1c); (1d); (1e); (1f); (1g); or (1h); R_6 is a direct bond; a straight-chain or branched C_1 - C_4 alkylene radical or a radical of formula (a) or (b); R_7 , R_8 and R_9 are each independently of one another C_1 - C_{18} alkyl; C_1 - C_{18} alkoxy or a radical of formula (1i); R_{10} , R_{11} and R_{12} are each independently of one another C_1 - C_{14} alkyl which is unsubstituted or substituted by one or several OH groups; R_{13} is hydrogen; M; C_1 - C_5 alkyl; or a radical of formula (c) R_{14} is C_1 - C_5 alkyl; M is a metal cation; T_1 is hydrogen; or C_1 - C_8 alkyl; m_1 is 1 to 3; m_2 is 2 to 14; and p_1 is 0; or a number from 1 to 5, for protecting human and animal skin and hair from the damaging effect of UV radiation. The compounds used according to this invention are very powerful UVA absorbers with fractions in the UVB range and are particularly suitable as sunscreens in cosmetic, pharmaceutical and veterinary compositions.



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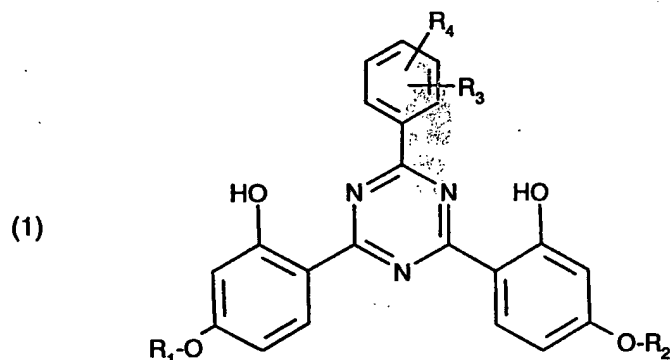
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Cosmetic use of bis(resorcinyl)triazine derivatives

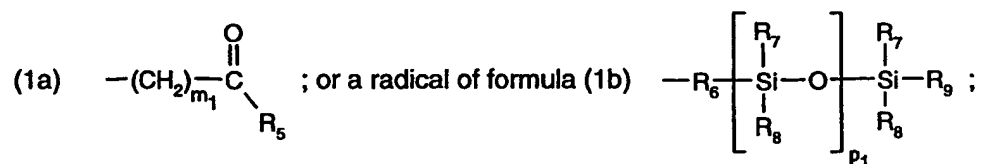
The present invention relates to the use of selected bis(resorcinyl)triazine derivatives for protecting human and animal skin and hair from the damaging effect of UV radiation and to a cosmetic formulation comprising these bis(resorcinyl)triazine derivatives.

The bis(resorcinyl)triazines used according to this invention correspond to formula



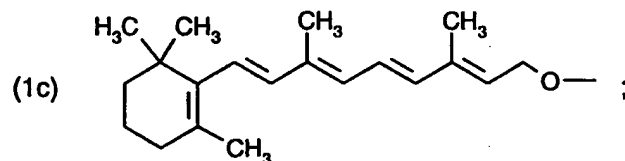
wherein

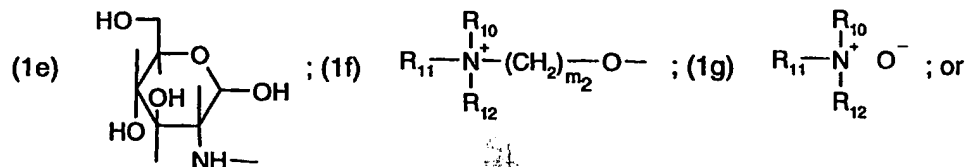
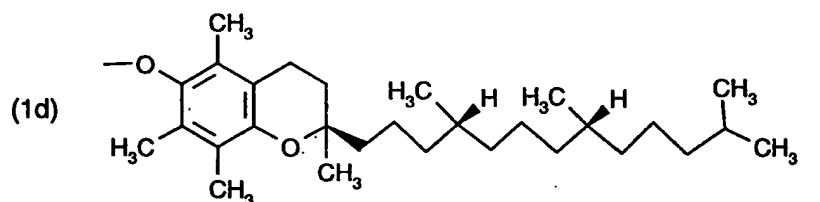
R_1 and R_2 are each independently of the other hydrogen; branched C_5 - C_{18} alkyl; C_2 - C_{18} alkenyl; a radical of formula $-CH_2-CH(OH)-CH_2-O-T_1$; a radical of formula



R_3 and R_4 are each independently of the other hydrogen or C_1 - C_5 alkyl;

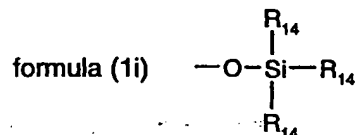
R_5 is hydroxy; C_1 - C_5 alkoxy which is unsubstituted or substituted by one or several OH groups; amino; mono- or di- C_1 - C_5 alkylamino; M; a radical of formula





R_6 is a direct bond; a straight-chain or branched C_1 - C_4 alkylene radical or a radical of formula $-C_{m_1}H_{2m_1}-$ or $-C_{m_1}H_{2m_1}O-$;

R_7 , R_8 and R_9 are each independently of one another C_1 - C_{18} alkyl; C_1 - C_{18} alkoxy or a radical of



R_{10} , R_{11} and R_{12} are each independently of one another C_1 - C_{14} alkyl which is unsubstituted or substituted by one or several OH groups;

R_{13} is hydrogen; M; C_1 - C_5 alkyl; or a radical of formula $-(CH_2)_{m_2}-O-T_1$;

R_{14} is C_1 - C_5 alkyl;

M is a metal cation;

T_1 is hydrogen; or C_1 - C_8 alkyl;

m_1 is 1 to 3;

m_2 is 2 to 14; and

p_1 is 0; or a number from 1 to 5.

C_1 - C_5 Alkyl, C_1 - C_8 alkyl and C_1 - C_{18} alkyl are straight-chain or branched alkyl radicals, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl, isoamyl or tert-amyl,

heptyl, octyl, isooctyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

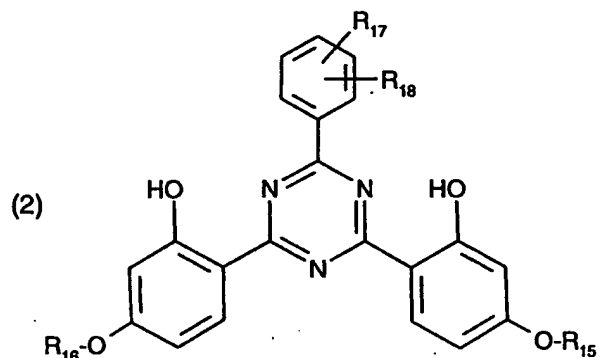
C₁-C₅Alkoxy and C₁-C₁₈alkoxy are straight-chain or branched alkoxy radicals, such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butyloxy, sec-butyloxy, tert-butyloxy, amyloxy, isoamyloxy or tert-amyloxy, heptyloxy, octyloxy, isooctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy or octadecyloxy.

C₂-C₁₈Alkenyl is, for example, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, iso-dodecenyl, n-dodec-2-enyl or n-octadec-4-enyl.

Examples of mono- or di-C₁-C₅alkylamino are methylamino, ethylamino, propylamino, n-butylamino, sec-butylamino, tert-butylamino, pentylamino, dimethylamino, diethylamino; dipropylamino; dibutylamino or methylethylamino.

Examples of metal cations are the lithium, potassium, sodium, calcium, magnesium, copper or zinc ion.

According to this invention, it is preferred to use bis(resorciny) compounds of formula



wherein

R₁₅ and R₁₆ are each independently of the other branched C₅-C₁₈alkyl; or -CH₂-CH(-OH)-CH₂-O-T₁;

R₁₇ and R₁₈ are each independently of the other hydrogen or C₁-C₅alkyl; and T₁ is hydrogen; or C₁-C₅alkyl.

Preeminently interesting compounds are those of formula (2), wherein

R_{15} and R_{16} are each independently of the other branched C_5 - C_{18} alkyl or $-CH_2-CH(-OH)-CH_2-O-T_1$;

R_{17} and R_{18} are hydrogen; and

T_1 is hydrogen; or C_1 - C_5 alkyl;

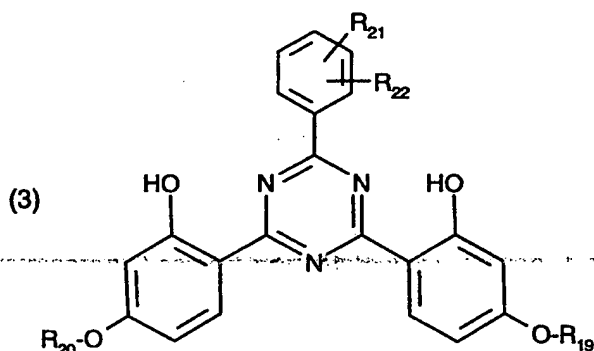
and in particular those compounds of formula (2), wherein

R_{15} and R_{16} are each independently of the other branched C_5 - C_{18} alkyl; and

R_{17} and R_{18} are hydrogen.

Very particularly preferred are those triazine compounds of formula (2), wherein R_{15} and R_{16} have the same meaning.

Other triazine derivatives which may be used according to this invention are those corresponding to formula



wherein

R_{19} and R_{20} are each independently of the other the radical of formula $-CH_2-C(=O)-O-R_{23}$; and

R_{21} , R_{22} and R_{23} are each independently of one another hydrogen; or C_1 - C_{10} alkyl.

Examples to be mentioned of compounds of formula (1) are:

2-(4'-methylphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine;

2-(2',4'-dimethylphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine;

2-phenyl-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine;

2-phenyl-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine;

2-phenyl-4-[[4-(3-(2-propyloxy)-2-hydroxypropyloxy)-2-hydroxy]phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine;

2-(4'-methylphenyl)-4,6-bis[[4-(2-ethylhexyloxy)-2-hydroxy]phenyl]-1,3,5-triazine;

2-(2',4'-dimethylphenyl)-4,6-bis[[4-(2-ethylhexyloxy)-2-hydroxy]phenyl]-1,3,5-triazine;

2-phenyl-4,6-bis[[4-(2-ethylhexyloxy)-2-hydroxy]phenyl]-1,3,5-triazine;

2-phenyl-4,6-bis[[4-(tris(trimethylsiloxy)silylpropyloxy)-2-hydroxy]phenyl]-1,3,5-triazine;

2-phenyl-4,6-bis[[4-(2-methylpropenyloxy)-2-hydroxy]phenyl]-1,3,5-triazine;

2-phenyl-4,6-bis[[4-(3-(2-propyloxy)-2-hydroxypropyloxy)-2-hydroxy]phenyl]-1,3,5-triazine; or

2-phenyl-4,6-bis[[4-(2-ethylhexyloxy)-2-hydroxy]phenyl]-1,3,5-triazine.

Other examples of triazine derivatives are listed in Table 1:

Table 1:		
R_a	R_b	R_c
H		
CH ₃		
H		
CH ₃		
H	-OH	-OH

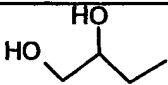
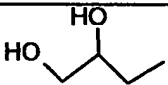
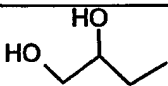
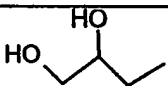
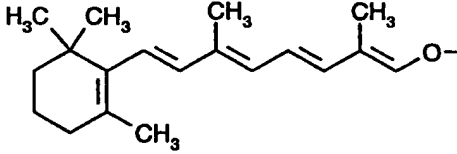
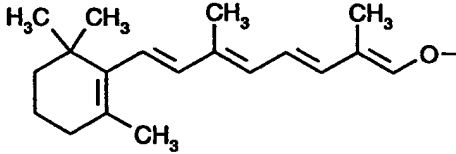
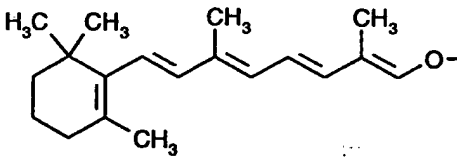
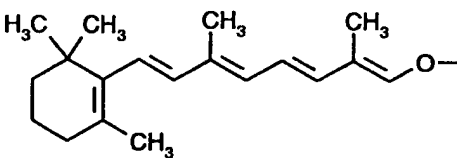
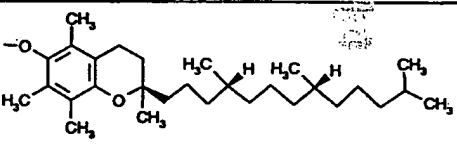
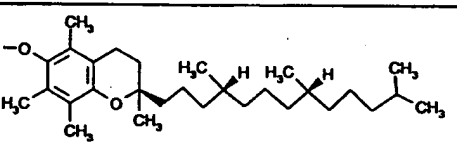
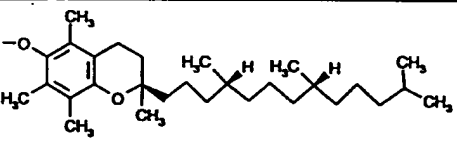
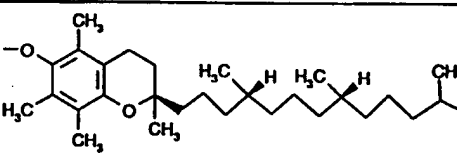
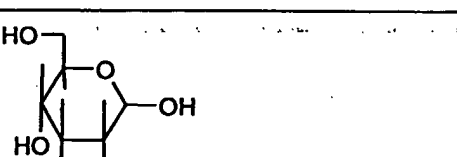
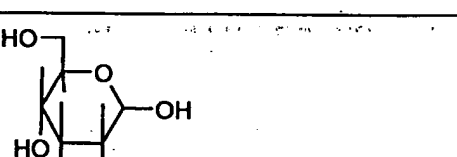
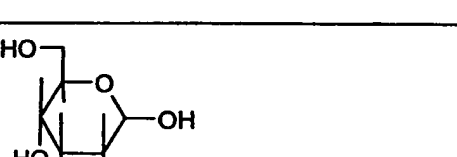
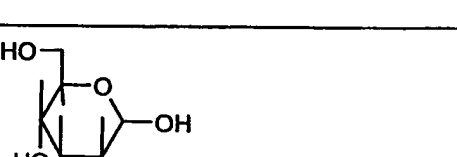
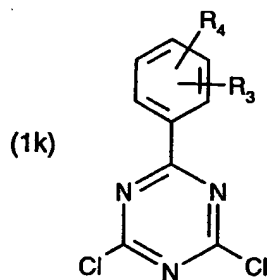
Table 1 (continuation)		
<u>R_a</u>	<u>R_b</u>	<u>R_c</u>
CH ₃	-OH	-OH
H	-OH	-OH
H	-OM M= alkali metal, alkaline earth metal, Cu, Zn, Mg	-OM M= alkali metal, alkaline earth metal, Cu, Zn, Mg
CH ₃	-OM M= alkali metal, alkaline earth metal, Cu, Zn, Mg	-OM M= alkali metal, alkaline earth metal, Cu, Zn, Mg
H	O ⁻ + N(CH ₂ CH ₂ OH) ₃	O ⁻ + N(CH ₂ CH ₂ OH) ₃
CH ₃	O ⁻ + N(CH ₂ CH ₂ OH) ₃	O ⁻ + N(CH ₂ CH ₂ OH) ₃
H	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{N}^+-(\text{CH}_2)_n-\text{O}- \\ \\ \text{CH}_3 \end{array}$ n=2-14	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{N}^+-(\text{CH}_2)_n-\text{O}- \\ \\ \text{CH}_3 \end{array}$ n=2-14
CH ₃	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{N}^+-(\text{CH}_2)_n-\text{O}- \\ \\ \text{CH}_3 \end{array}$ n=2-14	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{N}^+-(\text{CH}_2)_n-\text{O}- \\ \\ \text{CH}_3 \end{array}$ n=2-14
H		
CH ₃		
H		

Table 1 (continuation)		
<u>R_a</u>	<u>R_b</u>	<u>R_c</u>
CH ₃		
H		
CH ₃		
H		
CH ₃		

The bis(resorcynyl)triazines which may be used in accordance with this invention can be prepared in different manner, for example using aromatic nitrile compounds as starting compounds. The dichlorotriazine compound of formula



can be prepared, for example, by reacting benzonitrile with dicyandiamide to the diamino-triazine compound which is subsequently saponified to the dihydroxytriazine (tautomer = -dione) and then converted to the dichlorotriazine compound of formula (1k) with thionyl chloride. The two resorcinol groups are then introduced in commonly known manner by Friedel-Crafts acylation of resorcinol in the presence of a Lewis acid, preferably aluminium chloride. In the third step, the free hydroxyl groups in p-position are etherified, depending on the meaning of R_1 and R_2 in the compound of formula (1) by alkylation or acid-catalysed addition of glycidyl ethers.

Other processes for the preparation of the triazine derivatives which can be used in accordance with this invention are described in EP-A-0,775,698.

The bis(resorciny)l triazine compounds of formula (1) used according to this invention are particularly suitable as UV filters, i.e. for protecting ultraviolet-sensitive organic materials, in particular human and animal skin and hair, from the harmful effect of UV radiation. These compounds are, in particular, very powerful UVA absorbers with fractions in the UVB range and can be produced at low cost. Accordingly, these compounds are suitable for use as light stabilisers in cosmetic, pharmaceutical and veterinary compositions. They can be used in dissolved as well as in micronised state.

Accordingly, this invention also relates to a cosmetic formulation, which comprises at least one compound of formula (1) as well as cosmetically compatible carriers or auxiliaries.

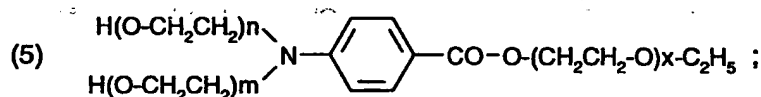
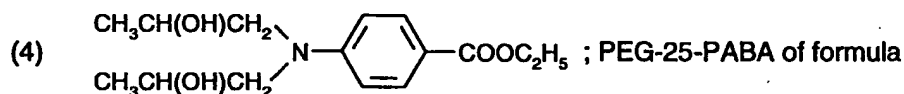
For cosmetic use, the light stabilisers of this invention usually have an average particle size in the range from 0.02 to 2, preferably from 0.05 to 1.5 and, most preferably, from 0.1 to 1.0 μ m. The insoluble UV absorbers used according to this invention can be brought to the desired particle size by customary methods, for example by grinding e.g. with a jet, ball, vibratory or hammer mill. Grinding is preferably carried out in the presence of 0.1 to 30 by

weight, preferably of 0.5 to 15 % by weight, based on the UV absorber, of a grinding aid such as an alkylated vinylpyrrolidone polymer, vinylpyrrolidone-vinylacetate copolymer, acylglutamate or, preferably, phospholipid.

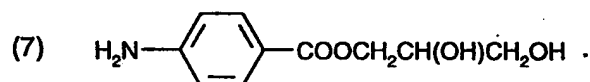
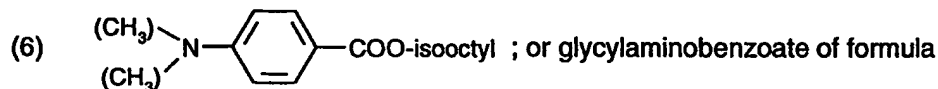
In addition to the inventive UV absorbers, the cosmetic formulation can also contain one or more than one other UV protective, for example an organic UV absorber from the classes of the p-aminobenzoic acid derivatives, salicylic acid derivatives, benzophenone derivatives, dibenzoylmethane derivatives, diphenylacrylate derivatives, benzofuran derivatives, polymeric UV absorbers comprising one or more than one organosilicon radical, cinnamic acid derivatives, camphor derivatives, trianilino-s-triazine derivatives, phenylbenzimidazolesulfonic acid and the salts thereof, menthylantranilates, benzotriazole derivatives, and/or an inorganic micropigment selected from the group consisting of aluminium oxide- or silicium dioxide-coated TiO_2 , zinc oxide or mica.

- Examples of p-aminobenzoic acid derivative compounds:

4-aminobenzoic acid (PABA); ethyldihydroxypropyl-PABA of formula

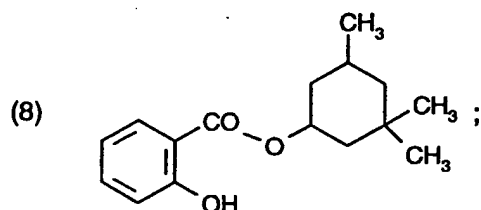


wherein m, n and x have the same meaning and are each at most 25;
octyldimethyl PABA of formula

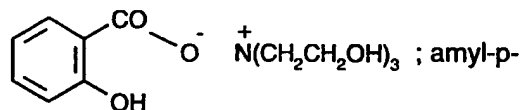


- Examples of salicylic acid derivative compounds:

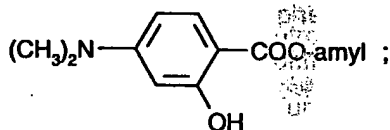
homomenthylsalicylate of formula



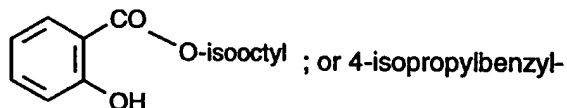
triethanolaminosalicylate of formula (9)



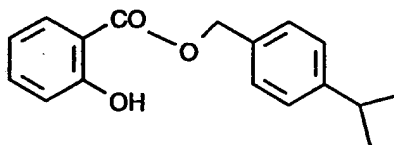
dimethylaminobenzoate of formula (10)



octylsalicylate of formula (11)



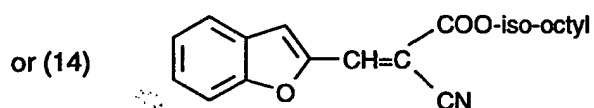
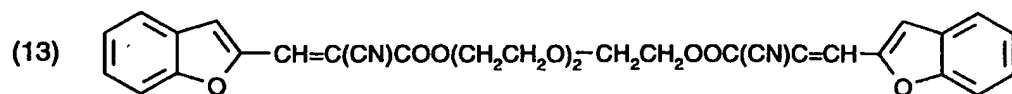
salicylate of formula (12)



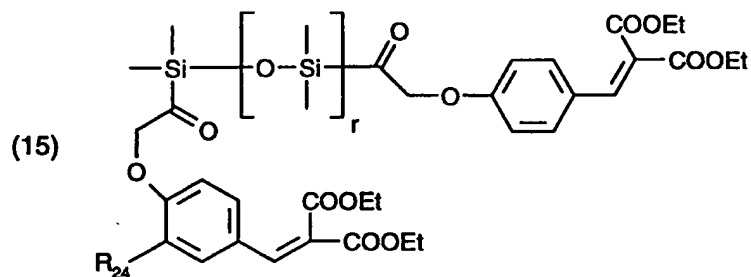
- Examples of benzophenone derivative compounds:
benzophenone-3-(2-hydroxy-4-methoxybenzophenone), benzophenone-4-(2-hydroxy-4-methoxybenzophenone-5-sulfonic acid) or benzophenone-8-(2,2'-dihydroxy-4-methoxybenzophenone).
- Examples of dibenzoylmethane derivative compounds:
butylmethoxydibenzoylmethane[1-(4-tert-butyl)-3-(4-methoxyphenyl)propane-1,3-dione].
- Examples of diphenylacrylate derivative compounds:
octocrylene(2-ethylhexyl-2-cyano-3,3'-diphenylacrylate) or etocrylene(ethyl-2-cyano-3,3'-diphenylacrylate).

- Examples of benzofuran derivative compounds:

3-(benzofuranyl)-2-cyanoacrylate, 2-(2-benzofuranyl)-5-tert-butylbenzoxazole or 2-(p-aminophenyl)benzofurane and, in particular, the compound of formula



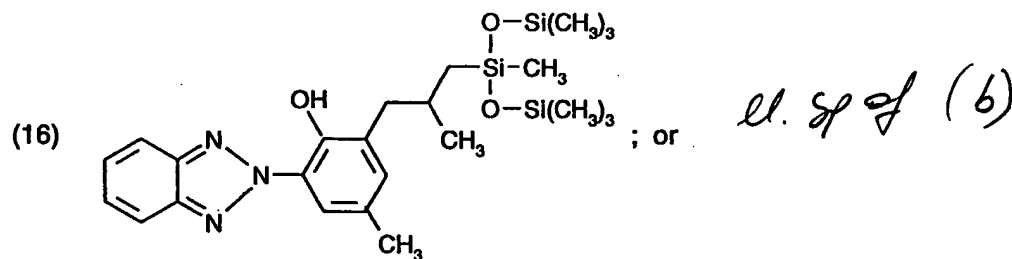
benzylidenemalonate derivative, in particular the compound of formula

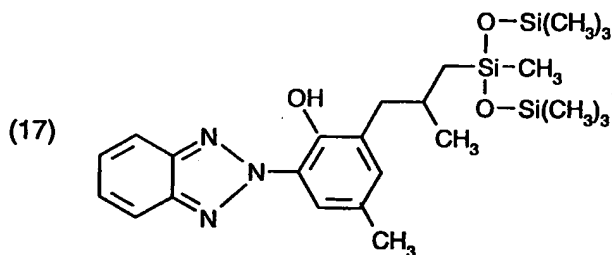


wherein

R₂₄ is hydrogen or O-Me and

r is approximately 7; the compound of formula





- Examples of cinnamate compounds:
octylmethoxycinnamate (4-methoxycinnamic acid-2-ethylhexyl), diethanolaminomethoxycinnamate (the diethanolamine salt of 4-methoxycinnamic acid), isoamyl-p-methoxycinnamate (4-ethoxycinnamic acid-2-isoamyl), 2,5-diisopropylmethylcinnamate or a cinnamic acid amido derivative.
- Examples of camphor derivative compounds:
4-methyl-benzylidenecamphor [3-(4'-methyl)benzylidenebornan-2-one], 3-benzylidenecamphor (3-benzylidenebornan-2-one), polyacrylamidomethylbenzylidenecamphor {N-[2(and 4)-2-oxyborn-3-ylidenemethyl]benzyl]acrylamide polymer}, trimoniumbenzylidenecamphorsulfate-[3-(4'-trimethylammonium)benzylidenebornan-2-onemethylsulfate], terephthalylidenedicamphorsulfonic acid {3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxobicyclo-[2.2.1]heptane-1-methanesulfonic acid) or the salts thereof, or benzylidenecamphorsulfonic acid [3-(4'-sulfo)benzylidenebornan-2-one] or the salts thereof.
- Examples of trianilino-s-triazine derivative compounds:
octyltriazine-[2,4,6-trianilino-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine, and also the trianilino-s-triazine derivatives disclosed in US-A-5,332,568, US-A-5,252,323, WO 93/17002 and WO 97/03642 and EP-A-0,517,104.
- Examples of benzotriazole compounds:
2-(2-hydroxy-5-methylphenyl)benzotriazole.

The novel cosmetic formulation comprises 0.1 to 15 by weight, preferably 0.5 to 10 % by weight, based on the total weight of the formulation, of a UV absorber or of a mixture of UV absorbers as well as a cosmetically compatible auxiliary.

The cosmetic formulation can be prepared by physically mixing the UV absorber(s) with the auxiliary by customary methods, for example by simply stirring the individual components together.

The novel cosmetic formulation can be formulated as water-in-oil or oil-in-water emulsion, as oil-in-alcohol lotion, as vesicular dispersion of a ionic or nonionic amphiphilic lipid, as gel, solid stick or as aerosol formulation.

As water-in-oil or oil-in-water emulsion, the cosmetically compatible auxiliary preferably comprises 5 to 50% of an oil phase, 5 to 20% of an emulsifier and 30 to 90% of water. The oil phase can contain any oil suitable for cosmetic formulations, for example one or more than one hydrocarbon oil, wax, natural oil, silicone oil, fatty acid ester or fatty alcohol. Preferred mono- or polyols are ethanol, isopropanol, propylene glycol, hexylene glycol, glycerol and sorbitol.

It is possible to use any conventional emulsifier for the inventive cosmetic formulation, for example one or more than one ethoxylated ester of natural derivatives, such as polyethoxylated ester of hydrogenated castor oil; or a silicone oil emulsifier such as silicone polyol; an optionally ethoxylated fatty acid soap; an ethoxylated fatty alcohol; an optionally ethoxylated sorbitan ester; an ethoxylated fatty acid; or an ethoxylated glyceride.

The cosmetic formulation can also contain other components, for example emollients, emulsion stabilisers, skin moisturisers, suntan accelerators, thickeners such as xanthane, moisture retention agents such as glycerol, preservatives, fragrances and colourants.

The novel cosmetic formulation is distinguished by excellently protecting the human skin against the harmful effect of sunlight.

In the following Examples percentages are by weight. The amounts given for the bis(resorcinyl)triazine compounds refer to the pure substance.

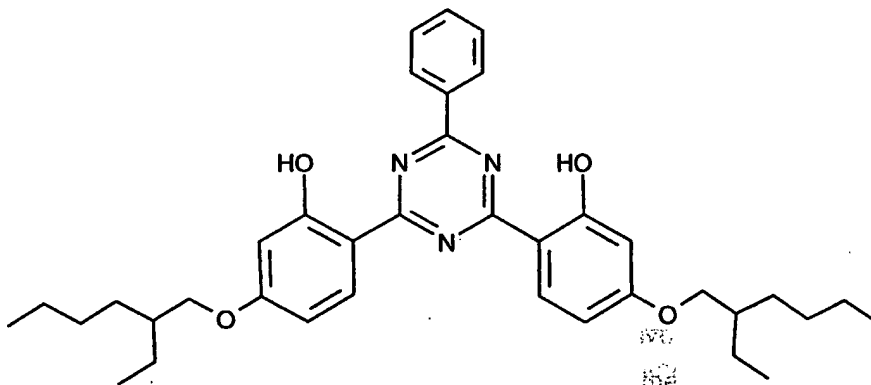
Examples:Use Examples for cosmetic light protection

The light stabilisers are determined in accordance with the method of Diffey and Robson, J. Soc. Cosmet. Chem. 40, 127 - 133 (1989) using an SPF analyser (Optometrix, SPF 290).

To determine the photostabilities, the filter substances are dissolved in ethanol ($c = 1 \cdot 10^{-5} - 5 \cdot 10^{-5} \text{ M}$) and irradiated, with stirring, in a quartz cuvette using a metal halide lamp (Macam) ($I_{UVB} = 0.4 - 8.0 \text{ mW/cm}^2$). To convert to the solar spectrum (CIE D65-norm daylight, standardised to $I_{UVB} = 0.127 \text{ mW/cm}^2$), the integral over the products of the wavelength-resolved lamp intensity and the corresponding absorption values of the respective UV absorbers from 290 to 400 nm is calculated and is then divided by the integral over the products of the D65 light intensities and the corresponding absorption values of the respective UV absorber in the range from 290 to 400 nm. This factor is multiplied with the half life period for degradation under metal halide lamp irradiation to obtain the corresponding half life period under solar irradiation. The half life period for the photodegradation under lamp irradiation is determined via UV-spectroscopic measurement of the extinction at the wavelength of the maximum absorption and subsequent exponential fit. Using the process described, the half life periods for the photodegradation in D65 light are thus obtained.

Example 1: o/w emulsion with the compound of formula (101)

(101)

 λ_{max} : 356 nm (ethanol) ϵ_{max} : 41 400 M⁻¹cm⁻¹(A):

triazine UV absorber of formula (101)	4 g
sesame oil	10 g
glyceryl stearate	4 g
stearic acid	1 g
cetyl alcohol	0.5 g
Polysorbate 20	0.2 g

(B):

propylene glycol	4 g
propylparaben	0.05 g
methylparaben	0.15
triethanolamine	0.1 g
Carbomer 934	0.1 g
water	ad 100 ml

Preparation of the emulsionPhase (A):

The UV absorber is first dissolved in sesame oil and the other components of (A) are then added and fused together.

Phase (B):

Propylparaben and methylparaben are dissolved in propylene glycol. 60ml water are then added, the mixture is heated to 70°C and Carbomer 934 is emulsified therein.

Emulsion:

(A) is slowly added to B with vigorous mechanical energy input. The volume is adjusted to 100 ml by addition of water.

The sunscreen factors and photostabilities obtained are compiled in Table 1.

<u>Table 1:</u>	<u>Concentration</u>	<u>Sunscreen factor *)</u>	<u>Photostability**)</u> <u>[h]</u>
compound of formula (101)	4%	7.1	6000

*) according to Diffey and Robson

**) as half life period of the photodegradation in D65 light in ethanolic solution

The sunscreen factor can be varied via the UV absorber concentration.

The results demonstrate that the active substance has high photostability and that a good sunscreen factor may be achieved even at low concentration.

Other physically defined measures for UVA characterisation:

Table 2: Other physically defined measures for UVA characterisation

	<u>compound of formula (101)</u> <u>4% emulsion</u>
T(360) ¹	0.6 %
UVA/UVB ratio ²	0.79
λ_{crit} [nm] ³	373

Example 2: Sunscreen Emulsion containing new oil soluble filter (101) and Octyl methoxycinnamate

<u>Phase</u>	<u>Component</u>	<u>% b.w.</u>
(A)	Water (aqua), deionized	54.90
	Xanthan gum, 2% solution	15.00
	Propylene glycol	1.50
	Tetrasodium EDTA	0.10
(B)	Isopropylmyristate	10.00
	Triazine UV-absorber with formula (101)	3.00
(C)	Octyl methoxycinnamate	7.50
	Glyceryl stearate (and) PEG-100 stearate	3.00
	Cyclomethicone	1.00
	Cetearyl alcohol (and) cetareth-20 (Amerchol)	3.00
(D)	Propylene glycol (and) methylparaben (and) propylparaben (and) diazolidinyl urea (ISP)	1.00

¹ Transmission at 360 nm

² Ratio of the areas standardised to the wavelengths under the absorption curve from 290 to 320 and from 320 to 400 nm

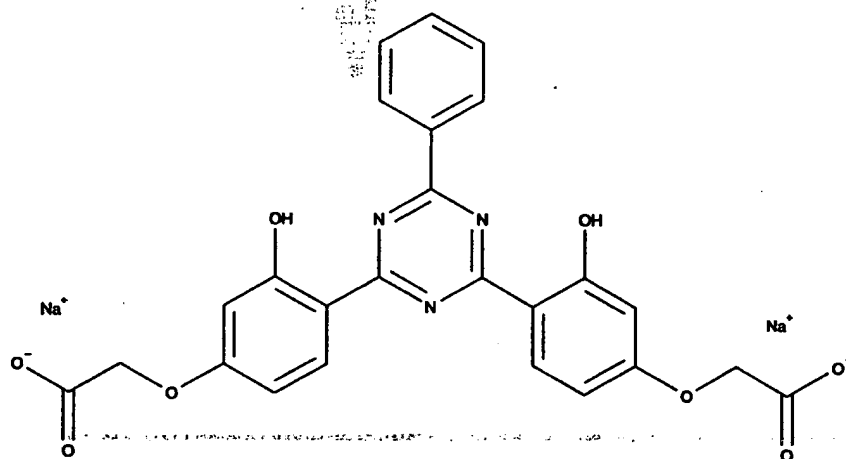
³ Wavelength at which 90% of the area under the absorption curve is reached when starting the integration at 290 nm and defining the area between 290 and 400 nm as 100%.

Procedure: The components of (A) are mixed in order and heated to 75°C. Components of (B) are mixed, heated to 75°C and stirred until filter is dissolved. Then (C) is added to B and mixed for 20 minutes (= mixture (BC)). (D) is then added to (BC) (= mixture (BCD)). (A) is added to (BCD) while mixing and cooling to room temperature.

Resulting SPF (Sun Protection Factor): 16 (method according example 1)

Example 3: Sunscreen Formulation containing new water soluble filter of the formula (102) and Octyl methoxycinnamate

(102)



$\lambda_{\max} = 352\text{nm}$ (ethanol)

$\epsilon_{\max} = 39\,800\text{ M}^{-1}\text{ cm}^{-1}$

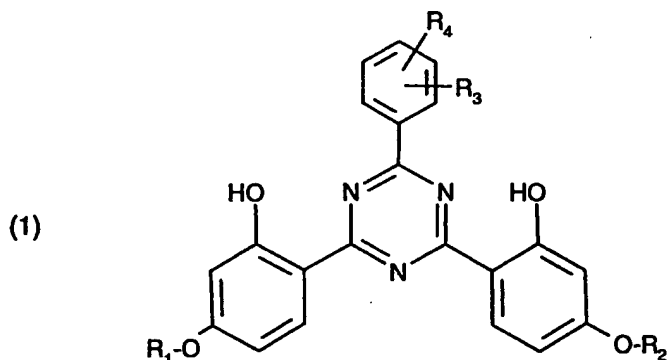
<u>Phase</u>	<u>Component</u>	<u>% b.w.</u>
(A)	Triazine UV-absorber with formula (102)	4.00
	Carbomer	0.30
(B)	water (aqua), deionized	57.93
(C)	Propylene glycol	5.00
	Methylparaben	0.20
	Propylparaben	0.10
	Triethanolamine	0.45
	Tetrasodium EDTA	0.02
(D)	Octyl methoxycinnamate	5.00
	Glyceryl stearate (and) PEG-100 stearate	1.00
	Cyclomethicone	5.00
	Glyceryl stearate	4.00
	Stearic acid	2.50
	Isostearyl isostearate	10.00
	Hydrogenated castor oil	2.00
	C ₁₂₋₁₅ alkyl benzoate	2.50

Procedure: (A) is dispersed in (B) and, when uniform, components of (C) (= mixture (ABC)) are added in order. While heating to 85°C, components of (D) are combined in a separate vessel and heated with mixing to 85°C. When (ABC) and (D) are both at 85°C and uniform, (D) is slowly added to ABC with strong mixing. 15 minutes after the last of D has been added cooling batch is started and cool to room temperature.

Resulting SPF (Sun Protection Factor): 12 (method according example 1)

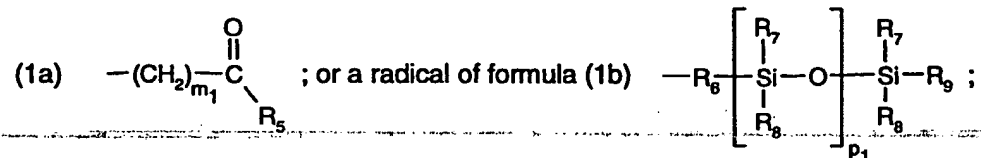
What is claimed is

1. Use of a UV absorber of formula



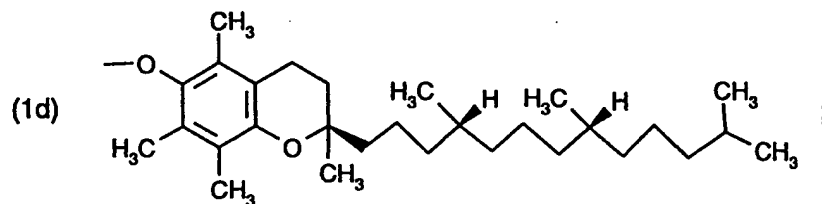
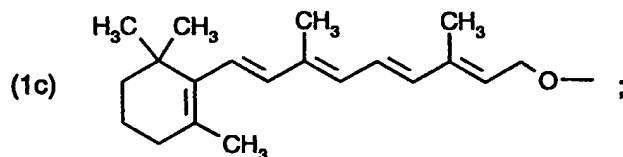
wherein

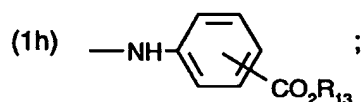
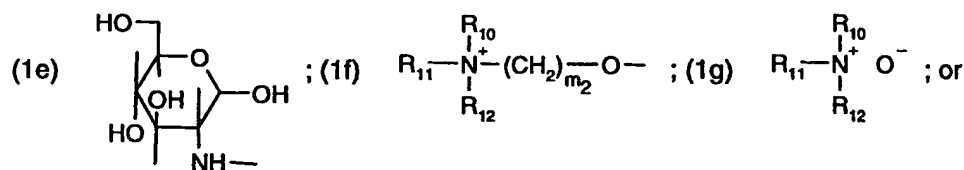
R_1 and R_2 are each independently of the other hydrogen; branched C_5 - C_{18} alkyl; C_2 - C_{18} alkenyl; a radical of formula $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-T_1$; a radical of formula



R_3 and R_4 are each independently of the other hydrogen or C_1 - C_5 alkyl;

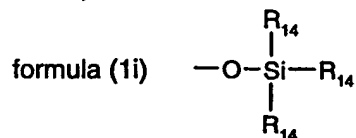
R_5 is hydroxy; C_1 - C_5 alkoxy which is unsubstituted or substituted by one or several OH groups; amino; mono- or di- C_1 - C_5 alkylamino; M; a radical of formula





R_6 is a direct bond; a straight-chain or branched C_1 - C_4 alkylene radical or a radical of formula $-C_{m_1}H_{2m_1}-$ or $-C_{m_1}H_{2m_1}O-$;

R_7 , R_8 and R_9 are each independently of one another C_1 - C_{18} alkyl; C_1 - C_{18} alkoxy or a radical of



R_{10} , R_{11} and R_{12} are each independently of one another C_1 - C_{14} alkyl which is unsubstituted or substituted by one or several OH groups;

R_{13} is hydrogen; M; C_1 - C_5 alkyl; or a radical of formula $-(CH_2)_{m_2}-O-T_1$;

R_{14} is C_1 - C_5 alkyl;

M is a metal cation;

T_1 is hydrogen; or C_1 - C_8 alkyl;

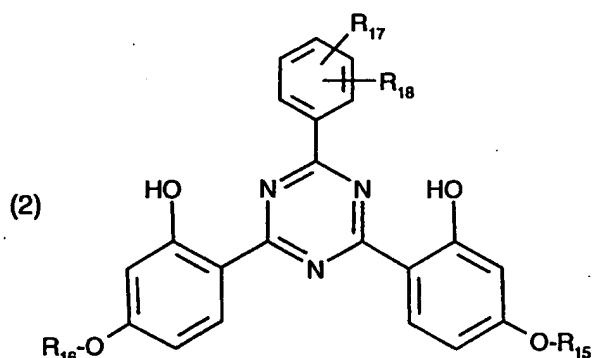
m_1 is 1 to 3;

m_2 is 2 to 14; and

p_1 is 0; or a number from 1 to 5,

for protecting human and animal skin and hair from the damaging effect of UV radiation.

2. Use according to claim 1, wherein the bis(resorcinyl)triazine used is the compound of formula



wherein

R_{15} and R_{16} are each independently of the other branched C_5 - C_{18} alkyl or $-CH_2-CH(-OH)-CH_2-O-T_1$;

R_{17} and R_{18} are hydrogen; and

T_1 is hydrogen; or C_1 - C_5 alkyl.

3. Use according to claim 2, wherein, in formula (2),

R_{15} and R_{16} are each independently of the other C_1 - C_{18} alkyl or $-CH_2-CH(-OH)-CH_2-O-T_1$;

R_{17} and R_{18} are hydrogen; and

T_1 is hydrogen; or C_1 - C_5 alkyl.

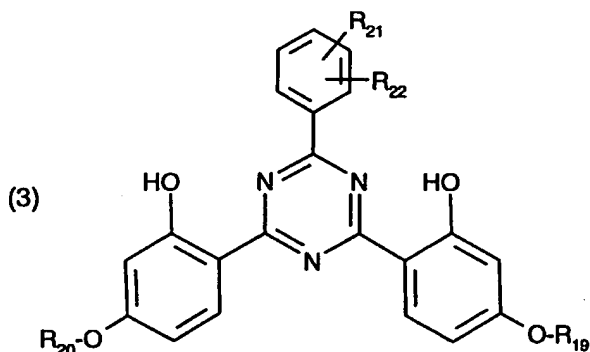
4. Use according to claim 3, wherein, in formula (2),

R_{15} and R_{16} are each independently of the other branched C_5 - C_{18} alkyl; and

R_{17} and R_{18} are hydrogen.

5. Use according to any one of claims 2 to 4, wherein R_{15} and R_{16} in formula (2) have the same meaning.

6. Use according to claim 1, which comprises using a bis(resorciny)triazine of formula



wherein

R_{19} and R_{20} are each independently of the other the radical of formula $-\text{CH}_2-\text{C}(\text{O})\text{O}-R_{23}$; and

R_{21} , R_{22} and R_{23} are each independently of one another hydrogen; or $\text{C}_1\text{-C}_{10}$ alkyl.

7. A cosmetic formulation, which comprises a UV absorber of formula (1) according to claim 1 together with cosmetically compatible carriers or auxiliaries.

8. A formulation according to claim 7, which comprises additional UV protectives.

9. A formulation according to either claim 7 or claim 8, wherein the additional UV protectives are an organic UV absorber from the classes of the p-aminobenzoic acid derivatives, salicylic acid derivatives, benzophenone derivatives, dibenzoylmethane derivatives, diphenylacrylate derivatives, benzofuran derivatives, polymeric UV absorbers comprising one or more than one organosilicon radical, cinnamic acid derivatives, camphor derivatives, trianilino-s-triazine derivatives, phenylbenzimidazolesulfonic acid and the salts thereof, menthylantranilates, benzotriazole derivatives, and/or an inorganic micropigment selected from aluminium oxide- or silicium dioxide-coated TiO_2 , zinc oxide or mica.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/05042

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CH 480 090 A (CIBA) 31 October 1969 see the whole document	1-9
A	BE 639 329 A (CIBA) see the whole document	1-9
A	BE 650 932 A (CIBA) 25 January 1965 see the whole document	1-9
A	EP 0 775 698 A (CIBA SPECIALTY CHEMICALS HOLDING) 28 May 1997 cited in the application see the whole document	1-9
A	WO 95 22959 A (CIBA-GEIGY) 31 August 1995 see the whole document	1-9
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

14 December 1998

Date of mailing of the international search report

18/12/1998

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Fischer, J.P.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/05042

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 0 878 469 A (CIBA SPECIALTY CHEMICALS HOLDING) 18 November 1998 see the whole document -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/05042

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CH 480090	A	31-10-1969	NONE	
BE 639329	A		BE 639330 A CH 467833 A DE 1215712 B DE 1216874 B FR 1379138 A FR 1381452 A GB 1033387 A GB 1033388 A NL 123744 C NL 299880 A NL 299881 A SE 315891 B SE 315892 B US 3242175 A	01-03-1965 19-03-1965 13-10-1969 13-10-1969 22-03-1966
BE 650932	A	25-01-1965	CH 469053 A DE 1291511 B FR 1405559 A GB 1065425 A NL 6408514 A SE 316470 B US 3249608 A	22-11-1965 27-01-1965 27-10-1969 03-05-1966
EP 775698	A	28-05-1997	DE 19543730 A AU 7194696 A JP 9188666 A NZ 299786 A SG 45516 A	28-05-1997 29-05-1997 22-07-1997 24-09-1998 16-01-1998
WO 9522959	A	31-08-1995	AU 1665395 A BR 9506935 A EP 0746305 A GB 2286774 A, B JP 9509421 T ZA 9501459 A	11-09-1995 09-09-1997 11-12-1996 30-08-1995 22-09-1997 23-08-1995
EP 878469	A	18-11-1998	AU 6598798 A	19-11-1998